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The influence of environmental factors on the carbon dioxide flux across the water–air interface of reservoirs in south-eastern Poland

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ABSTRACT

Studies concerning the emission of carbon dioxide (CO₂) were carried out in 2009–2012 for six reservoirs located in four provinces of south-eastern Poland. The CO₂ flux across the water–air interface was measured using the “static chamber” method. The measured fluxes of CO₂ (FCO₂) ranged from –30.64 to 183.78 mmol/m²/day, and the average values varied in the range from –3.52 to 82.11 mmol/m²/day. In most of the cases, emission of CO₂ to the atmosphere was observed. The obtained values of CO₂ fluxes were comparable to values typical for other temperate reservoirs. Analysis of the influence of selected environmental factors on the FCO₂ showed that it depends on parameters characterizing both the sediments and surface water. The CO₂ flux at the water–air interface was positively correlated with parameters of bottom sediments such as porosity, content of organic carbon and total nitrogen; and negatively with pH value and δ¹³C of organic carbon. In the case of the parameters characterizing surface water, positive dependences on the concentrations of nitrate and total nitrogen, and negative relationships with water temperature and chlorophyll *a* concentrations, were found.

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Introduction

Carbon dioxide (CO₂) is the most important anthropogenic greenhouse gas, whose concentration in the atmosphere is growing systematically, causing an increase in average air temperature. The global concentration of CO₂ in the atmosphere has increased from the pre-industrial value of about 280 ppm to 379 ppm in 2005. If these trends continue, they could have a negative influence on the environment and socio-economic factors (IPCC, 2007).

Therefore, studies concerning the emission of this gas from various anthropogenic sources are being carried out worldwide. One of these sources is reservoirs located in different climatic zones. During reservoir damming, a certain

area of land, which is covered with vegetation, is flooded. Furthermore, in an existing reservoir, organic matter is produced in the process of primary production and delivered from the catchment. The thus accumulated organic material dies and is deposited in the bottom sediments, where it is decomposed by bacteria. In the presence of oxidants, the organic matter is mineralized, and the final product of this process is, among others, CO₂. Under anaerobic conditions, the organic matter is degraded by fermentation, and CO₂ and CH₄ are the gaseous end products of this process. The amount of CO₂ transported into the atmosphere via the water–air interface is not equivalent to the amount produced in the sediment, and depends on many factors. For example, methanogenesis (reduction of CO₂) and photosynthesis

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processes are sinks for CO₂. Furthermore, CO₂ can be produced in the water column during mineralization of organic matter as well as absorbed from the atmosphere.

The main aim of the research was obtaining information on the CO₂ flux at the water – air interface from selected reservoirs and analysis of the factors controlling this flux.

1. Material and methods

1.1. Study area

The research was conducted between 2009 and 2011, from spring to autumn. Six reservoirs located in four provinces of south-eastern Poland were selected for the study: (reservoirs in Podkarpackie Province: Rzeszów — 50° 2' 1" N, 22° 0' 17" E, Maziarnia — 50° 21' 0" N, 21° 55' 59" E and Besko — 49° 33' 10" N, 21° 55' 56" E; reservoir in Lubelskie province: Nielisz — 50° 48' 1" N, 23° 2' 38" E; reservoir in Świętokrzyskie province: Chańcza — 50° 40' 25" N, 21° 2' 48" E; reservoir in Małopolskie province: Klimkówka — 49° 33' 8" N, 21° 5' 16" E) (Fig. 1). The reservoirs selected differed in size, age, degradation level, and also the influence of anthropogenic pollution. In Table 1 characteristic parameters of the studied reservoirs are shown.

In each reservoir, the studies were conducted at two stations (Fig. 1) located in the shallow parts of the reservoir. Their depth, depending on the water level, ranged from 0.5 to 1.0 m. The stations R1, M1, B1, N1, C1 and K1 were located in the shallow parts of the inflow area, and the stations R2, M2, B2, N2, K2 and C2 in the upper parts of the reservoirs.

1.2. Measurement of carbon dioxide flux at the water–air interface

The CO₂ fluxes were estimated using a “static chamber” method. A stainless-steel chamber (0.3 m × 0.3 m × 0.16 m) equipped with a dry battery driven fan and a small vent stopped by a silicone septum for sampling was used. Five gas samples from the chamber air headspace were manually withdrawn into gastight syringes at 0, 10, 20, 30, and 40 min after deployment. All samples were transported to the laboratory, and the gas concentration was analyzed within 4 hr. The samples were analyzed using a Pye Unicam gas chromatograph (GC, model PU-4410/19) equipped with a flame ionization detector (FID) and a stainless steel column packed with Haye Sep. Q, 80/100 Mesh, 6 ft. in length and 2 mm ID. The GC was also equipped with a methanizer to detect low levels of CO₂. The methanizer is packed with a nickel catalyst

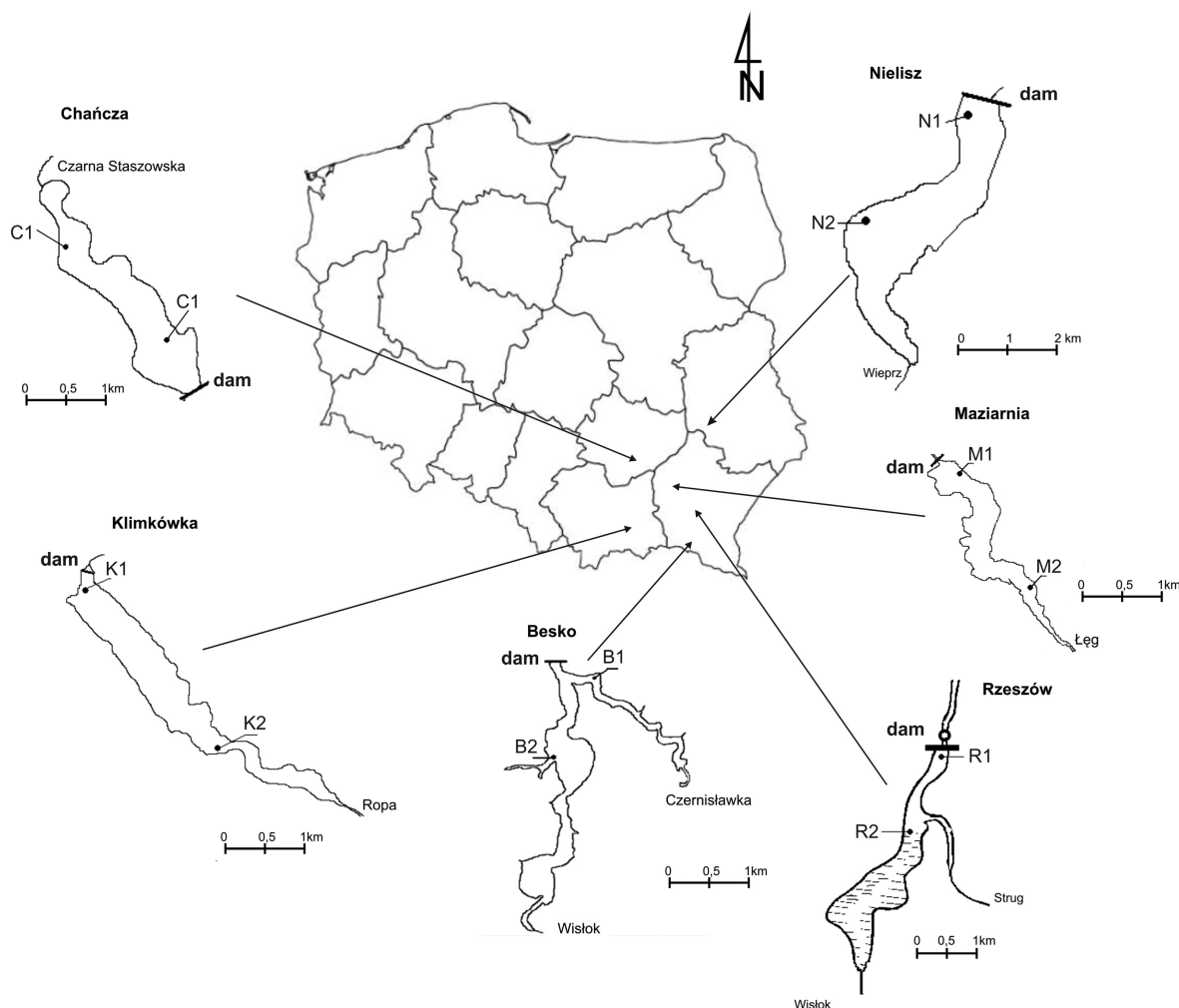


Fig. 1 – Localization of the studied reservoirs with sampling stations.

Table 1 – Selected parameters of the studied reservoirs.

Reservoir	Rzeszów	Maziarnia	Besko	Nielisz	Chańcza	Klimkówka
Voivodeship	Podkarpackie	Podkarpackie	Pokarpackie	Lubelskie	Świętokrzyskie	Małopolskie
River	Wisłok	Łęg	Wisłok	Wieprz	Czarna Staszowska	Ropa
Commissioning year	1974	1988	1978	2008	1984	1994
Volume (mln m ³)	0.5	4.2	15.4	19.5	24.2	43.5
Area (ha)	41.6	160	124.5	890	340	310
Max. depth (m)	6	8	30	4	11	30
Mean depth (m)	0.5	2.6	12	2	4.17	13
Retention time (days)	2	36	61	–	218	148
Catchment area (km ²)	2050	–	207	–	475	210
Catchment character	Mountain	Lowland	Mountain	Lowland	Lowland	Mountain

powder and heated to 380°C. When the column effluent mixes with the FID hydrogen supply and passes through the methanizer, CO₂ is converted to CH₄. The carrier gas was helium at a flow rate of 30 cm³/min.

Gas fluxes (expressed in mmol/m²/day) were calculated from a linear regression of the gas concentration change within the chamber versus time, taking into account the surface and volume of the chamber. Positive changes indicated emission of gas from the reservoir, while negative changes indicated its consumption.

1.3. Surface water analysis

Temperature (*t_w*), pH and dissolved oxygen (O₂) were measured in situ with a MultiLine P4 meter (WTW, Germany). Nitrate (N-NO₃⁻) and phosphates (P-PO₄³⁻) were determined spectrophotometrically (Photolab S12, WTW, Germany) in filtered samples of water (N-NO₃⁻ – the salicylate method, P-PO₄³⁻ – reaction with ammonium molybdate). Total phosphorus (TP) and total nitrogen (TN) were determined analogously to nitrates and phosphates, but in non-filtered and mineralized samples of water. Chlorophyll *a* was determined spectrophotometrically (Photolab S12, WTW, Germany) after hot extraction with ethanol.

1.4. Sediment analysis

Sediment cores were taken from the littoral zone using a gravity sediment corer (KC Kajak of Denmark). In the top (1 cm) layer of the sediment, porosity, pH, total organic carbon (TOC), TN and δ¹³C of organic carbon were measured.

For porosity measurements, the water content per volume of sediment was determined by drying a known volume of the wet sediment to a constant weight at 105°C. The pH of sediment in the suspension with 1 mol/L KCl was determined potentiometrically with a MultiLine P5 meter (WTW, Germany).

Before the analysis of TOC, TN and δ¹³C, carbonates were removed from the samples by 72 hr contact with the vapor of 30% HCl in desiccators (Zimmermann et al., 1997). The TOC and TN concentrations were subsequently measured using a CN analyzer (CN Flash EA 1112, ThermoQuest) at 1020°C. Blank and standard samples with known elemental composition (sulfanilamide) were used for quality control. The precision of the method was approximately ±3%. Stable isotopic composition of the organic carbon was determined using an IRMS DELTA^{Plus} Finnigan system connected with a

CN analyzer (CN Flash EA 1112, ThermoQuest). The isotopic ratios were reported in standard δ-notation (δ¹³C) expressed as “per mil”: δ¹³C (‰) = (¹³C/¹²C_(sample) / ¹³C/¹²C_(standard) – 1) × 10³, relative to the PDB standard. The method was calibrated using National Bureau of Standards 22 (NBS 22) for δ¹³C. The precision of measurements was ±0.1‰.

1.5. Statistical analysis

For the obtained results, basic descriptive statistics such as the minimum, maximum, mean and standard deviation values were calculated. The MS Excel 2007 program was used for calculations. For linear relationships, Pearson's correlation coefficient with the corresponding level of significance *p* was calculated. The Student's *t*-test was used to compare means for the two groups, and a non-parametric Kruskal–Wallis test was used to estimate differences between a few groups. The multiple regression analysis method was used to determine the simultaneous influence of a few (at least two) independent variables on a dependent variable. It was performed using the Statistica 10 PL Statistical Package. Significance was defined as *p* < 0.05.

2. Results and discussion

2.1. Characteristics of the analyzed water and sediment

Table 2 presents the observed ranges of changes in the chosen parameters of waters and bottom sediments of the examined reservoirs.

Depending on the season and the weather conditions, the measured temperature of the surface water ranged from 8.0 to 28.0°C. The dissolved oxygen concentration of the water varied from 1.74 to 10.60 mg/dm³, which was equivalent to saturation from 20% to 120%. Both the lowest and the highest saturation levels were observed in summer when the water temperature and insolation were the highest. All the analyzed waters were slightly alkaline, with the pH value varying according to the season from 7.34 to a value greater than 9.00.

The concentration of nitrate in the studied water ranged from 0.036 mg/dm³ to almost 2 mg/dm³, while the concentration of TN ranged from 1.017 to 4.436 mg/dm³. Concentrations of phosphates and total phosphorus ranged from 0.003 mg/dm³ to 1.440 mg/dm³ and from 0.04 to 1.815 mg/dm³, respectively. The maximum values of P-PO₄³⁻ and TP in the water of Rzeszów, Maziarnia and Nielisz reservoirs were noted only once, in June

Table 2 – Range of some parameters of the surface water and the surface (1 cm) layer of bottom sediment in the studied reservoirs.

Parameter	Rzeszów	Maziarnia	Besko	Nielisz	Chańcza	Klimkówka
Water						
t_w (°C)	8.0–28.0	12.0–24.4	14.3–24.9	13.5–26.7	19.4–23.3	15.0–22.7
O_2 (mg/dm ³)	1.74–9.22	3.12–9.21	6.83–8.82	5.80–10.60	5.88–7.85	7.23–9.96
Reaction (pH)	7.34–9.06	7.36–8.75	8.36–9.21	7.62–8.93	8.61–8.72	7.90–8.43
N-NO ₃ ⁻ (mg/dm ³)	0.104–1.966	0.168–1.534	0.329–0.962	0.036–0.765	0.632–1.045	0.691–0.815
TN (mg/dm ³)	1.260–3.564	1.482–3.847	1.592–2.078	1.017–4.436	2.064–3.178	1.444–1.856
P-PO ₄ ³⁻ (mg/dm ³)	0.010–1.406	0.012–1.401	0.004–0.017	0.007–1.440	0.003–0.067	0.020–0.032
TP (mg/dm ³)	0.088–1.528	0.079–1.429	0.043–0.059	0.079–1.815	0.040–0.084	0.041–0.085
Chl <i>a</i> (µg/dm ³)	0.10–112.54	2.96–86.38	5.18–15.55	11.85–159.19	19.25–21.47	0.74–5.18
Sediment						
Porosity (cm ³ /cm ³)	0.79–0.99	0.35–0.99	0.58–0.96	0.50–0.99	0.50–0.56	0.82–0.98
Reaction (pH)	7.04–7.42	5.08–7.80	7.57–7.70	7.20–7.99	7.83–8.13	5.65–6.40
TOC (%)	1.61–4.39	0.08–5.90	0.48–0.91	0.21–4.77	0.11–0.40	0.30–0.69
TN (%)	0.12–0.37	0.01–0.59	0.03–0.07	0.02–0.23	0.01–0.03	0.03–0.08
δ ¹³ C (‰)	–29.20– –22.62	–29.76– –26.99	–20.24– –4.11	–26.53– –15.77	–28.19– –25.41	–24.56– –24.14

2010. This was a period after high rainfall and floods, so the elevated values of phosphates and TP were directly connected with the increased surface runoff. Apart from this one case, the concentration of phosphates and TP remained at a relatively constant level. As in the case of the concentrations of different forms of nitrogen, no significant changes were observed in connection with changing seasons. The concentration of chlorophyll *a* in the water of reservoirs varied from 0.1 to over 159 µg/dm³. The lowest primary production expressed as the concentration of chlorophyll *a* was noted in Klimkówka reservoir, and the highest in Nielisz reservoir.

The analyzed bottom sediments differed visually both between the reservoirs and also in some cases between research stations within one reservoir. Stations M1, N1, C1 and C2 were characterized by sandy sediments with low porosity. In other cases, the porosity of sediments rose to as high as 99%. The pH value of sediments varied from 5.08 to 8.13. The highest acidity was seen in the sediments taken from the bottom of reservoirs Maziarnia and Klimkówka. The concentration of organic carbon in the surface level of the studied bottom sediments was relatively low and ranged from 0.08% to 5.9%. The lowest value was noted at the M1 station, and the highest at the M2 station. Except for the M2 station of the Maziarnia reservoir, the bottom sediments of the Rzeszów reservoir were the richest in organic matter. A low value for organic matter was found in all the sandy sediments, thus at the M1 station of Maziarnia reservoir, at the C1 and C2 stations of Chańcza reservoir and at the N1 station of Nielisz reservoir. In the surface layer of analyzed sediments, the content of total nitrogen ranged from 0.01% to 0.59%. Similar to the case with organic carbon, the highest value of this indicator was noted at the M2 station in Maziarnia reservoir, and the lowest values were obtained in the case of sediments taken from the bottom of Chańcza reservoir. The isotopic composition of organic carbon expressed in terms of δ¹³C ranged from –29.76‰ to –4.11‰ and indicated the mixed character (auto- and allochthonous) of organic matter deposited in the studied sediments.

2.2. Diffusion fluxes of CO₂ at the water–air interface

Characteristic values of the CO₂ fluxes at the water–air interface (FCO₂) for the studied reservoirs are presented in Table 3, and the seasonal changes are shown in Fig. 2.

The FCO₂ in Rzeszów reservoir ranged from 11.49 to 183.78 mmol/m²/day. The average FCO₂ at the R1 station was 48.85 mmol/m²/day, and at the R2 station FCO₂ was higher, yielding an average value of 72.24 mmol/m²/day. The differences between the stations were statistically significant ($t = -1.213$; $df = 25$; $p = 0.236$). In the Maziarnia reservoir, the FCO₂ ranged from –4.70 to 138.33 mmol/m²/day. The negative value, indicating absorption of CO₂ from the atmosphere, occurred only once (July 2011) at the M1 station. In June of the same year and at the same station, neither the release nor absorption of CO₂ was observed. In other cases, emission of CO₂ to the atmosphere was observed. Statistically significant differences between the stations were found ($t = -2.272$; $df = 14$; $p = 0.039$). The FCO₂ in the Besko reservoir was lower compared to the reservoirs at Rzeszów and Maziarnia. In spring, at both stations, absorption of CO₂ from the atmosphere was observed. In the summer and autumn, FCO₂ was lower and ranged from 6.40 to 10.58 mmol/m²/day. The average value for B1 and B2 stations was –3.52 and 4.99 mmol/m²/day, respectively. The FCO₂ in the Nielisz reservoir was positive for the whole study and ranged from 3.58 to 84.54 mmol/m²/day. The differences between the stations were statistically significant ($t = -4.210$, $df = 14$, $p = 0.001$), and average values at the N1 and N2 stations were 15.70 and 52.93 mmol/m²/day, respectively. The FCO₂ in Chańcza reservoir was measured only twice in the year 2010 and ranged from 17.67 to 39.47 mmol/m²/day. In the Klimkówka reservoir, FCO₂ ranged from –9.92 to 46.78 mmol/m²/day. The average values at K1 and K2 stations were 5.43 and 28.16 mmol/m²/day, respectively.

Summarizing, the FCO₂ ranged from –30.64 to 183.78 mmol/m²/day, while the average values of the flux in the studied reservoirs were in the range from –3.52 to

Table 3 – Minimum, maximum and average values of carbon dioxide fluxes at the water – air interface.

Reservoir	Station	CO ₂ (mmol/m ² /day)		
		Min.	Max.	Average ± SD
Rzeszów	R1 (n = 12)	11.49	162.51	48.85 ± 42.50
	R2 (n = 15)	13.27	183.78	72.24 ± 54.85
Maziarnia	M1 (n = 8)	–4.70	96.70	35.73 ± 40.49
	M2 (n = 8)	29.05	138.33	82.11 ± 41.15
Besko	B1 (n = 3)	–30.64	10.58	–3.52 ± 23.49
	B2 (n = 3)	–1.54	10.11	4.99 ± 5.95
Nielisz	N1 (n = 8)	3.58	52.48	15.70 ± 15.49
	N2 (n = 8)	22.96	84.54	52.93 ± 19.63
Chańcza	C1 (n = 2)	17.67	20.58	19.12 ± 2.05
	C2 (n = 2)	21.07	39.47	30.27 ± 13.01
Klimkówka	K1 (n = 2)	–9.92	20.78	5.43 ± 21.71
	K2 (n = 2)	9.55	46.78	28.16 ± 26.32

SD: standard deviation; n: number of measurements.

82.11 mmol/m²/day; however, the lowest average value was noted in the Besko reservoir, and the highest in the Maziarnia reservoir. In most of the cases the emission of CO₂ to

the atmosphere was observed. Only twice (in Nielisz and Klimkówka reservoirs) was absorption of this gas from the air noted.

A large variation in the FCO₂ was observed not only between studied reservoirs, but also within the measurements in a single reservoir. The non-parametric analysis of variance indicated statistically significant differences in the FCO₂ between the reservoirs (Kruskal-Wallis test: $H(5, N = 73) = 18.204$; $p = 0.003$) and enabled the division of the studied reservoirs into two groups. Rzeszów, Maziarnia and Nielisz are the reservoirs characterized by high FCO₂, but conversely Besko, Chańcza and Klimkówka are the reservoirs characterized by low FCO₂. Statistically significant differences in the FCO₂ between the stations were noted in the case of the Maziarnia reservoir ($t = -2.272$; $df = 14$; $p = 0.039$) and the Nielisz reservoir ($t = -4.210$; $df = 14$; $p = 0.001$).

According to St. Louis and others (2000), the values of diffusive CO₂ fluxes to the atmosphere from temperate reservoirs range from 17 to 70 mmol/m²/day (average approx. 32 mmol/m²/day), but values ranging from 10 to 232 mmol/m²/day (average approx. 79 mmol/m²/day) are characteristic of tropical reservoirs. Thus, it may be concluded that except for stations 2 in Rzeszów and

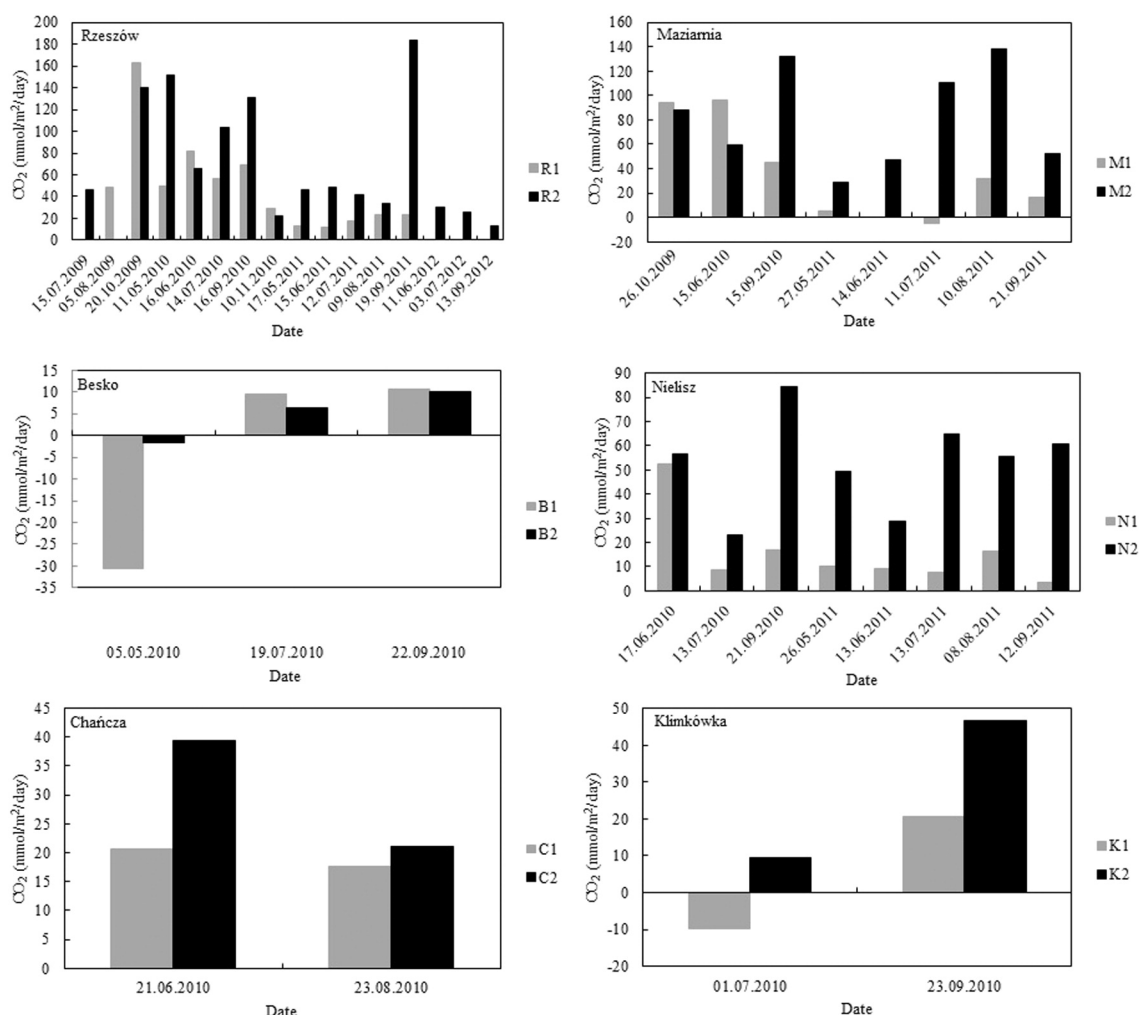


Fig. 2 – Seasonal changes of the carbon dioxide fluxes at the water–air interface in reservoirs of Rzeszów, Maziarnia, Besko, Nielisz, Chańcza, and Klimkówka.

Maziarnia reservoirs, the values of FCO_2 in the studied reservoirs were in the range of values characteristic of temperate reservoirs.

2.3. The influence of selected abiotic factors on the CO_2 flux at the water–air interface

For the three studied reservoirs (Rzeszów, Maziarnia and Nielisz) an analysis of the influence of chosen parameters of water and bottom sediments on FCO_2 was performed. Statistically significant relationships are presented in Fig. 3. The relationships involved both indicators characteristic of bottom sediments as well as those for surface water. The FCO_2 correlated positively with parameters of bottom sediments such as porosity, the content of organic carbon and total nitrogen concentration, and negatively with pH and the $\delta^{13}\text{C}$ values of organic carbon. As for the parameters characteristic of surface waters, positive correlation was found with the concentration of nitrates and total nitrogen, and negative correlation with the water temperature and chlorophyll *a* concentration.

To recognize the simultaneous influence of some parameters of water and bottom sediments on the FCO_2 , multiple regression analysis was performed (the data were normally distributed). The analysis showed that the value of the dependent variable in the function of independent variables was best described by the following equation:

$$\text{FCO}_2 = 44.42 + 39.08 \text{N-NO}_3 + 10.35 \text{TOC} - 2.29 t_w \pm 30.15$$

where, FCO_2 ($\text{mmol/m}^2/\text{day}$) is the flux of carbon dioxide at the water–air interface, N-NO_3 (mg/dm^3) is the concentration of nitrate in surface water, TOC (%) is the content of organic carbon in bottom sediments, and t_w ($^\circ\text{C}$) is the temperature of water.

As is apparent from the summary on the regression of the dependent variable (Table 4), the FCO_2 increased with increasing nitrate concentration in surface water and organic carbon content in the bottom sediments, whereas it decreased with increasing water temperature. An increase of nitrate concentration in water of approximately 1 mg/dm^3 and increase of organic carbon content in the sediments of approx. 1% caused FCO_2 increases about 39 and $10 \text{ mmol/m}^2/\text{day}$, respectively. Decrease in the water temperature of approx. one degree caused an increase of FCO_2 of approx. $2 \text{ mmol/m}^2/\text{day}$. Analysis of semi-partial correlation coefficients (Table 4) showed that the variable N-NO_3 explains almost 18% of the variation of the dependent variable after excluding the influence of other variables. For organic carbon content in the sediments and the temperature of water this value is 13% and 5%, respectively. The achieved model explains approx. 54% ($R^2 = 0.545$) of the variability of the FCO_2 . The high significance of the achieved parameters ($p < 0.000$) indicates good adjustment of the model. The accuracy of the model was additionally verified by analysis of relationships between independent variables included in the model. No statistically significant correlations were consistent with the assumptions of a multiple regression, which confirmed the correctness of the achieved model. Analysis of the normal distribution of residues also indicated the correctness of the model.

By analyzing data concerning emission of carbon greenhouse gases from the reservoirs mentioned in the literature in different climatic zones, one may state that one of the key factors influencing the magnitude of the emission of CO_2 from the surface of reservoirs is temperature. Reservoirs in the tropical zone, where temperatures are high, emit greater amounts of this gas than boreal reservoirs (St. Louis et al., 2000; Huttunen et al., 2003; Soumis et al., 2004; Demarty et al., 2009; Diem et al., 2012; Xiao et al., 2013). Changes of temperature can affect FCO_2 through influence on the solubility of CO_2 in water (Zhao et al., 2008), primary production and rate of organic carbon decomposition (Lü et al., 2007). Elevation in the water temperature promotes FCO_2 by increasing the decomposition rate of organic carbon. Furthermore, at higher temperatures the solubility of gases in water is lower, therefore increased emission of CO_2 to the atmosphere should be observed. Positive influence of temperature on the FCO_2 for reservoirs in different climatic zones was observed (Liikanen et al., 2002; Tremblay et al., 2005; Hirota et al., 2007; Rogério et al., 2013; Xiao et al., 2013; Kumar and Sharma, 2014). However, analyzing the research results presented in this paper, the negative influence of temperature was ascertained ($R^2 = 0.24$, $p < 0.001$) (Fig. 3). If algae are distributed in the water surface, elevation of the water temperature would promote CO_2 absorption because of the increase in the primary production of aquatic plants (Lü et al., 2007). Thus, the observed dependence suggests that at higher temperatures a greater amount of CO_2 was consumed in photosynthesis. This hypothesis may be confirmed by the relationship between the FCO_2 and the concentration of chlorophyll *a* in water (Fig. 3). For higher concentrations of chlorophyll *a*, lower FCO_2 was clearly observed, which indicates that this gas was consumed in the process of primary production. Other studies have also seen a negative relationship between FCO_2 and temperature for both temperate and tropical aquatic systems (Xing et al., 2005; Halbedel and Koschorreck, 2013; Rogério et al., 2013; Natchimuthu et al., 2014). Negative dependence on chlorophyll *a* was observed by Halbedel and Koschorreck (2013) and Zhao et al. (2013). As described above, the differential effect of temperature on the CO_2 flux at the water–air interface is observed both between reservoirs located in different regions and in the same climate zone. This suggests that the temperature is not the main factor limiting FCO_2 . Undoubtedly an increase in temperature accelerates microbial activity and thus the decomposition of organic matter, but other atmospheric factors such as a precipitation and wind speed can also have significant impact on the CO_2 emissions from reservoirs. Of enormous significance are also the chemical properties of sediments (especially the quantity and quality of organic matter) and water (e.g., oxygenation, content of nutrients, trophic state).

Another factor that undoubtedly has an effect on the flux of carbon greenhouse gases is the content of organic matter in the bottom sediments. CO_2 is one of the final products of organic matter decomposition, so greater abundance of organic matter in the bottom sediments will stimulate the production processes of this gas. Positive relationships between the carbon greenhouse gas flux and the content of organic matter or organic carbon in the bottom sediments is often described in the literature (Murase and Sugimoto,

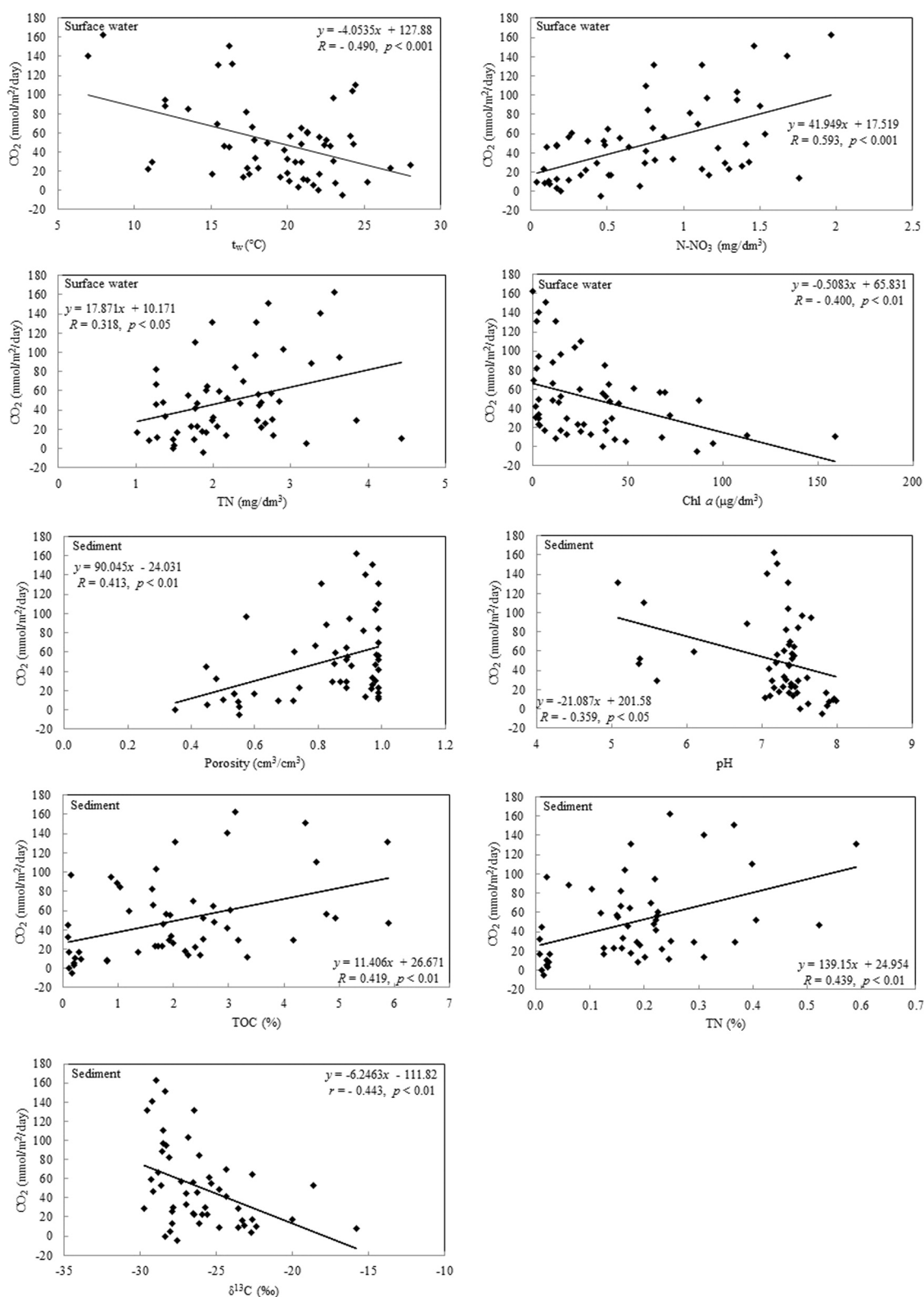


Fig. 3 – The relationships between the CO₂ flux at the water–air interface and selected parameters of surface water and bottom sediments (stations: R1, R2, M1, M2, N1, N2).

2001; Gruca-Rokosz et al., 2011; Schrier-Uijl et al., 2011; Furlanetto et al., 2012; Xiao et al., 2013; Gruca-Rokosz and Tomaszek, 2015). In the case of the studied reservoirs, statistically significant positive correlation was also found

between the content of organic carbon in the sediments and the FCO₂ (Fig. 3). A statistically significant correlation with the content of total nitrogen in sediments was also found; however, in Rzeszów and Maziarnia reservoirs, FCO₂

Table 4 – Results of multiple regression analysis.

	Coefficient B	Standard error of B	Significance level p	Semi-partial correlation	% variance
Intercept	44.41679	25.71578	0.040838		
Nitrate (N-NO ₃)	39.07607	9.24406	0.000111	0.420350	18
Total organic carbon (TOC)	10.34885	2.88032	0.000793	0.357285	13
Temperature of water (t _w)	−2.28615	1.06282	0.036762	−0.213898	5

R = 0.738, R² = 0.545, Standard error of estimation: 30.15, F(3,46) = 18.38, p < 0.0000.

was significantly correlated with organic carbon ($R^2 = 0.706$, $p < 0.001$ and $R^2 = 0.960$, $p < 0.001$, respectively), suggesting that most of the total nitrogen was organic nitrogen, which is a component of organic matter in the bottom sediments. Positive dependence between the content of total nitrogen in the bottom sediments and the FCO₂ was also described by Schrier-Uijl et al. (2011).

It is generally accepted that not only the quantity but also the quality of organic matter has an influence on the production of CO₂. Algae, which are part of autochthonous organic matter, decompose into CH₄ and CO₂ 10 times faster than lignocellulose (Benner et al., 1984), so the higher primary production accelerates the production of carbon greenhouse gases (Sepulveda-Jauregui et al., 2014). The present research determined the negative dependence of the FCO₂ from the $\delta^{13}\text{C}$ value, which is one of the indicators used for the estimation of the origin of organic matter (Fig. 3). Higher values of $\delta^{13}\text{C}$ characterize autochthonous organic matter (Hellings et al., 1999; Owen et al., 1999; Murase and Sakamoto, 2000), and due to the fact that this is the kind of organic matter more favorable for the production of carbon greenhouse gases (West et al., 2012), there was the expected positive dependence between this indicator and FCO₂. It should be mentioned that the obtained relationships concerned FCO₂, and it is known that CO₂ produced in the sediments is transported to the atmosphere with some loss, which is caused by consumption during photosynthesis. For example, in tropical reservoirs only 20% of CO₂ emitted to the atmosphere was produced in sediments, while the rest of it came from different sources (Abe et al., 2005).

The results of this study show also that the FCO₂ is negatively correlated with the pH of sediments (Fig. 3). However, no negative correlation was found between FCO₂ and the pH of water, which is often observed worldwide (Liikanen et al., 2002; Soumis et al., 2004; Tremblay et al., 2005; Schrier-Uijl et al., 2011; Peng et al., 2012; Halbedel and Koschorreck, 2013; Wang et al., 2013; Xiao et al., 2013; Yang et al., 2013; Kumar and Sharma, 2014). Alkaline water pH is conducive to creation of carbonates, which consequently reduces the saturation of water with CO₂. In such a situation, absorption of CO₂ from the atmosphere rather is more likely to be observed than emission (Tremblay et al., 2005).

In the studied reservoirs, statistically significant positive correlations were also found between the FCO₂ and the concentrations of nitrate and total nitrogen in surface water (Fig. 3). The observed dependencies are rather surprising, because a higher supply of biogenic compounds causes higher primary production. In such cases, the process of photosynthesis dominates over the process of respiration, and more CO₂ is consumed in the water column. Reduction of the

concentration of free CO₂, resulting from its uptake by organisms, causes an increase in the pH of water, which results from a shift of balance in the direction of HCO₃[−] and CO₃^{2−}. During highly productive days, the pH of water can increase to a value of even higher than 10 (Portielje and Lijklema, 1995). When the concentration of diluted, free CO₂ at the water–air interface is lower than the equilibrium concentration, then it can be absorbed from the atmosphere. So, the higher the concentration of biogenic compounds and in consequence higher trophic state of water, then the greater is the sink of CO₂, which causes eutrophic lakes to be potentially poorly saturated with carbon dioxide (Xing et al., 2005; Balmer and Downing, 2011; Trolle et al., 2012). Negative dependence between the CO₂ flux and nitrate was observed i.e., in the Nigerian reservoir Oyun (Kumar and Sharma, 2014), which may be a confirmation of the above considerations. However, in the literature can also be found information about positive correlations between the FCO₂ and the concentration of biogenic compounds such as: ammonium (Liikanen et al., 2003; Schrier-Uijl et al., 2011; Deshmukh, 2013; Halbedel and Koschorreck, 2013), phosphorus (Liikanen et al., 2003; Tundisi et al., 2008; Halbedel and Koschorreck, 2013) and total nitrogen (Tundisi et al., 2008). However, in Finnish lakes a positive dependence was observed between the concentration of CO₂ in water and the trophic state of these lakes (Kortelainen et al., 2006). The authors of the mentioned publications claim that trophic conditions strongly influence the carbon greenhouse gas flux at the water–air interface, and that the highest emission of CO₂ takes place in shallow, eutrophic reservoirs (Gunkel, 2009). It may be assumed that in well-oxygenated water of the studied reservoirs, nitrates come from the process of oxidation of ammonia, which is one of the products of decomposition of organic matter. So, the observed positive relationship between the FCO₂ and the concentration of nitrate can be an indirect reflection of the process of decomposition of organic matter, as a result of which CO₂ is produced.

3. Conclusions

The measured CO₂ fluxes at the water–air interface in studied reservoirs ranged from −30.64 to 183.78 mmol/m²/day. In this regard these reservoirs can be divided into two groups. Rzeszów, Nielisz and Maziarnia are reservoirs in which high CO₂ flux was observed; however, the other reservoirs were characterized by low flux of this gas. In most cases the values of CO₂ flux at the water–air interface were comparable to the characteristic values for reservoirs located in the temperate zone reported in the literature.

Analysis of the influence of abiotic factors on the CO₂ flux at the water–air interface showed that this flux was correlated positively with parameters of the bottom sediments such as porosity, content of organic carbon and total nitrogen, and negatively with pH and the value of $\delta^{13}\text{C}$ of organic carbon. In the case of parameter characteristic of surface water, the CO₂ flux was found to have a positive dependence on the concentrations of nitrate and total nitrogen and a negative relationship with the temperature of water and concentration of chlorophyll *a*.

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